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(71)出願人 000005108

株式会社日立製作所
東京都千代田区神田駿河台四丁目6番地

(72)発明者 鈴木 正徳

茨城県日立市久慈町4026番地 株式会社日立製作所日立研究所内

(72)発明者 永井 晃

茨城県日立市久慈町4026番地 株式会社日立製作所日立研究所内

(72)発明者 西村 伸

茨城県日立市久慈町4026番地 株式会社日立製作所日立研究所内

(74)代理人 弁理士 高田 幸彦

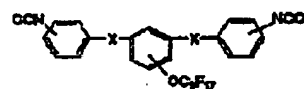
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(54)【発明の名称】 含フッ素シアネートを用いた硬化物及びそれを用いた積層板

(57)【要約】

【構成】一般式(1)

【化9】

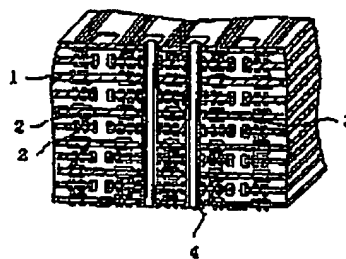


【1】

(式中、C、F、基は二重結合を一個有するパーフルオロノネニル基を、Xはエステル結合、あるいはエーテル結合を示す。)で表されるシアネート化合物を含むことを特徴とする熱硬化性樹脂組成物。

【効果】含フッ素シアネートから成る熱硬化性樹脂は成形性に優れ、かつ得られる硬化物は耐熱性、難燃性及び機械的特性に優れていることが確認でき、絶縁材料の電気特性として重要な比誘電率も小さくすることができる。

図 1



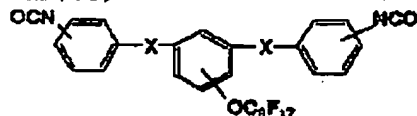
- 1... 樹脂板
- 2... 回路
- 3... プリプレグシート
- 4... スルーホール

特開平5-78448

(2)

【特許請求の範囲】

【請求項1】一般式(1)



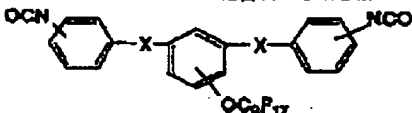
【1】

…(化1)

(式中、C₈F₁₇、基は二重結合を一個有するパーフルオ

ロノネニル基を、Xはエステル結合、あるいはエーテル

結合を示す。)で表されるシアネート化合物から成る樹

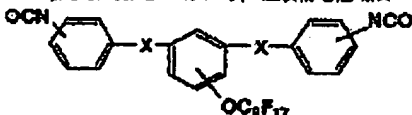


【1】

…(化2)

(式中、C₈F₁₇、基は二重結合を一個有するパーフルオ
ロノネニル基を、Xはエステル結合、あるいはエーテル
結合を示す。)で表されるシアネート化合物及び、マレ
イミド化合物、シアケイミド化合物、シアナト化合物、イ
ソシアナト化合物、エポキシ化合物、ビニル化合物及び
ポリ(p-ヒドロキシスチレン)誘導体の中の少なくと
も一種類から成る樹脂組成物。

【請求項3】請求項1または2において、組成物を溶融★



【1】

…(化3)

(式中、C₈F₁₇、基は二重結合を一個有するパーフルオ
ロノネニル基を、Xはエステル結合、あるいはエーテル
結合を示す。)で表されるシアネート化合物を含む樹脂
組成物を、多重結合の重合反応により三次元架橋して得
られる硬化物を用いた電気絶縁体。

【請求項7】請求項1または2において、前記樹脂組成
物を補強材である有機繊維布に含浸させて得られるブリ
ブレイク。【請求項8】請求項1または2に記載の前記樹脂組成物
を補強材である有機繊維布に含浸させて得られるブリ
ブレイク。【請求項9】請求項1または2に記載の前記樹脂組成物
を用いた積層材料。【請求項10】請求項1または2に記載の前記樹脂組成
物を他の樹脂成分と共に用いた積層材料。★に溶解して得られた均一なワニスを加熱重合して得られ
る硬化物。20 【請求項4】請求項1、2または3において、過酸化物
等のラジカル重合開始剤の存在下で重合させる硬化物。【請求項5】請求項1、2、3または4において比誘電
率が3以下である硬化物。

【請求項6】一般式(1)

【化3】

物を補強材である有機繊維布に含浸させて得られるブリ
ブレイクを積層積着して得られる積層材料。【請求項13】請求項1ないし12に記載の前記樹脂組
成物及び前記樹脂組成物を用いた積層材料により構成さ
れる配線板。【請求項14】請求項1ないし12に記載の前記樹脂組
成物及び前記樹脂組成物を用いた積層材料により構成さ
れる大面積基板。40 【請求項15】請求項1ないし12に記載の前記樹脂組
成物及び前記樹脂組成物を用いた積層材料により構成さ
れるモジュール基板。【請求項16】請求項1ないし12に記載の前記樹脂組
成物及び前記樹脂組成物を用いた積層材料により構成さ
れるマイクロチップキャリア基板。

【請求項17】請求項1ないし12に記載の前記樹脂組

v

(3)

特開平5-78446

【産業上の利用分野】本発明は含フッ素熱硬化性樹脂組成物にあり、特に、成形性、耐熱性及び、接着性に優れた低誘電率絶縁材料として好適な樹脂組成物に関する。

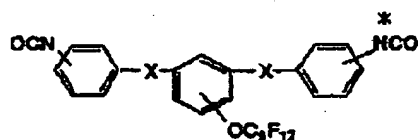
【0002】

【従来の技術】耐熱性をもつ熱硬化性樹脂組成物として従来ビスマレイミド等が用いられてきたがビスマレイミドにビスシアナミドを加えた組成物による樹脂は耐熱性、成形性が改善されることが見出されている。(特開昭58-71924号公報)しかし、これらの樹脂は分極率の大きいアミド基やイミド基を多数もつため比誘電率が比較的高いことが知られている。比誘電率の低い熱硬化性樹脂組成物は含フッ素マレイミド等を用いた樹脂が提案されているが(特開平2-73809号公報)フッ素を導入したことにより接着性が低下することが知られている。

【0003】また、低誘電率材料は、主として芳香族や環式脂肪族、またはこれらを組み合わせた分極の小さい構造をもつシアネート化合物(米国特許4,559,399号)や、イソシアネート化合物(米国特許4,353,769号)がある。しかし、シアネート化合物及びイソシアネート化合物は、難燃性が得られない(可燃性)と云う欠点がある。

【0004】そのため、信号の高速伝送の要求される大型計算機の高層プリント板に使用するためには接着性と比誘電率が小さく、かつ、難燃性を兼ね備えた材料が要求されている。

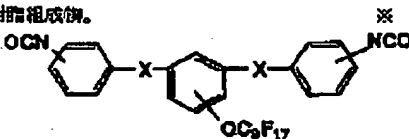
【0005】



【1】

…(化4)

【0011】(式中、C₆F₁₃、基は二重結合を一個有するパーフルオロネニル基を、Xはエステル結合、あるいはエーテル結合を示す。)で表されるシアネート化合物から成る樹脂組成物。



【1】

…(化5)

【0014】(式中、C₆F₁₃、基は二重結合を一個有するパーフルオロネニル基を、Xはエステル結合、あるいはエーテル結合を示す。)で表されるシアネート化合物

*【発明が解決しようとする課題】従来の熱硬化性樹脂の組成物は比誘電率を低下させる手段としてフッ素置換した官能基を導入していたが、この方法には金属との接着性が損われるという欠点がある。一般に、接着性を改善するためにはエステル等の官能基をもつ官能基を導入すれば良いことが知られているが、通常の方法では比誘電率が高くなる。

【0006】また、イソシアネート化合物やシアネート化合物は、触媒下で三量化して、架橋密度の高い硬化物を得ることが出来る。また、硬化物は比誘電率が低く、寸法安定性、耐熱性にも優れているが、プリント板として重要な特性である難燃性が得られないという欠点がある。

【0007】本発明の目的は耐熱性、接着性を損うことなく比誘電率が低く、さらに、難燃性の樹脂組成物を提供することにある。

【0008】

【課題を解決するための手段】本発明を要領すれば、極性をもつ官能基と共に、その導入による比誘電率の上昇を補えるような含フッ素シアネート化合物を用いることにより耐熱性、接着性を損うことなく比誘電率が低く、難燃性に優れた樹脂組成物を提供することができる。

【0009】(1) 一般式(1)

【0010】

【化4】

*【0012】(2) 一般式(1)

【0013】

【化5】

【0015】(3) 請求項1または2において組成物を溶媒に溶解して得られた均一なワニスを加熱重合して得られる硬化物。

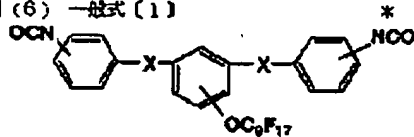
http://www.uspto.gov/patft/.../USPTO-Patent-Number=1115843660261

(4)

特開平5-78446

5
が3以下であることを特徴とする硬化物。

【0018】(6) 一般式(1)



*【0019】
【化6】

【1】

…(化6)

【0020】(式中、C、F、_n、_mは二重結合を一個有するパーフルオロネニル基を、Xはエステル結合、あるいはエーテル結合を示す。)で表されるシアネート化合物を含む樹脂組成物を、多重結合の重合反応により三次元架橋して得られる硬化物を用いた電気絶縁体。

【0021】(7) 請求項1または2に記載の樹脂組成物を補強材である有機繊維布に含浸させて得られるブリブレッグ。

【0022】(8) 請求項1または2に記載の樹脂組成物を補強材である有機繊維布に含浸させて得られるブリブレッグ。

【0023】(9) 請求項1または2に記載の樹脂組成物を用いた積層材料。

【0024】(10) 請求項1または2に記載の樹脂組成物を他の樹脂成分と共に用いた積層材料。

【0025】(11) 請求項1または2に記載の樹脂組成物を補強材である有機繊維布に含浸させて得られるブリブレッグを積層接着して得られる積層材料。

【0026】(12) 請求項1または2に記載の樹脂組成

10 物を補強材である有機繊維布に含浸させて得られるブリブレッグを積層接着して得られる積層材料。

【0027】(13) 請求項1ないし12に記載の樹脂組成物及び該組成物を用いた積層材料により構成される配線板

(14) 請求項1ないし12に記載の樹脂組成物及び該組成物を用いた積層材料により構成される大面積基板

(15) 請求項1ないし12に記載の樹脂組成物及び該組成物を用いた積層材料により構成されるモジュール基板

(16) 請求項1ないし12に記載の樹脂組成物及び該組成物を用いた積層材料により構成されるマイクロチップキャリア基板

(17) 請求項1ないし12に記載の樹脂組成物及び該組成物を用いた積層材料により構成されるピングリッドアレイ基板

本発明において一般式(1)で表される3-フルオロシアネート化合物は、例えば以下に示したものがある。

【0028】

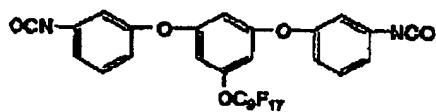
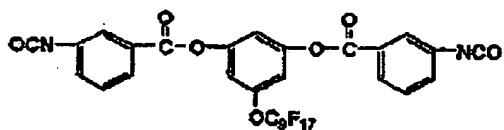
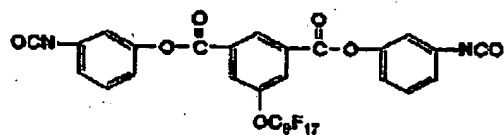
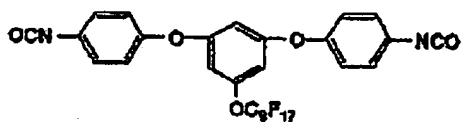
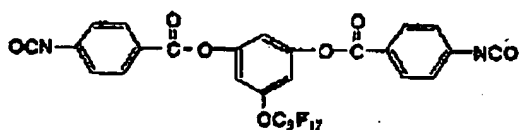
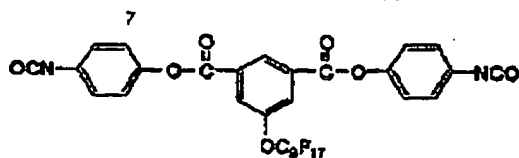
【化7】

<http://www.uspto.gov/patents/1008.2/patents/1008.2.html> ID=1115843675856

(5)

特開平5-78446

8



…(化7)

【0029】ただし、ここでC₆F₁₇基は、例えば、以
下に示したものがある。

【0030】
40 【化8】

$$\text{---C=C---CF}_2\text{CF}_2\text{CF}_2\text{---}$$

【作用】熱硬化性樹脂の接着性を向上させるために導入

1115843693998

11

て三次元架橋結合を構築するシアネート構造を保持することによって従来の特性を維持できた。更に、フッ素の含有率の高い置換基を導入することで耐燃性も優れた材料が得られた。

【0037】

【実施例】以下実施例により本発明を具体的に説明するが、本発明はこれらの実施例に限定されない。

【0038】（実施例1）2, 2-ビス（4-（4-シアネートフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン100gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いてプレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、溶融した後、250℃に昇温し加圧した。得られた樹脂板について特性評価した。比誘電率は、HewlettPackard社製LFインピーダンスアナライザ4192Aを用い、JIS-C-6481に従い試料の静電容量を測定し比誘電率を計算した。熱膨張率に関しては、真空型熱機械特性測定装置TM-3000を用い、樹脂板から7mm×7mmに切り出した試料の厚さ方向の熱膨張率（50～220℃）測定した。昇温速度2℃/min、荷重10gの圧縮モードで測定した。曲げ強度は島津製作所製オートグラフDDS-5000を用い、JIS-C-6481に従い測定した。樹脂板から50mm×5mmに切り出した試料について三点間隔30mm、たわみ速度2mm/minの条件で測定した。熱分解開始温度については、真空型熱重量測定器熱天秤TGD-7000RHを用いて測定した。樹脂成分を粉碎して得た、粉末試料10mgについて、He流量100cm³/minの雰囲気中、昇温速度5℃/minにおける加熱減重曲線を測定し5%減重を示す温度を熱分解開始温度とした。測定結果は表にまとめて示す。

【0039】（実施例2）2, 2-ビス（4-（4-シアネートフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン80gと2, 2-ビス（4-（4-マレイミドフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン（セントラル硝子）20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いてプレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、溶融した後、250℃に昇温し加圧した。得られた樹脂板の比誘電率、熱膨張率、

(7)

特開平5-78446

12

オロネニルオキシ-3, 5-フタロイルビス（4-（4-シアナミドフェノキシ）フェニル）（マナック）20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いてプレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、溶融した後、250℃に昇温し加圧した。得られた樹脂板の比誘電率、熱膨張率、曲げ強度、熱分解温度を測定した。

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【0041】（実施例4）2, 2-ビス（4-（4-シアネートフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン60gと2, 2-ビス（4-（4-マレイミドフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン（セントラル硝子）20gとポリ（p-ビニルプロモフェニルメタクリレート）（マナック）20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ（1-ブチルパーオキシ）-ヘキシン-3を0.2g加え、真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いてプレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、溶融した後、250℃に昇温し加圧した。得られた樹脂板の比誘電率、熱膨張率、曲げ強度、熱分解温度を測定した。

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【0042】（実施例5）2, 2-ビス（4-（4-シアネートフェノキシ）フェニル）-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン（セントラル硝子）80gと1-パーフルオロネニルオキシ-3, 5-フタロイルビス（4-（4-シアナミドフェノキシ）フェニル）（マナック）10g及び、ビスフェノールA型エポキシ化合物DER323（ダウケミカル）10gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いてプレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、溶融した後、250℃に昇温し加圧した。得られた樹脂板の比誘電率、熱膨張率、曲げ強度、熱分解温度を測定した。

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【0043】（比較例1）シアネート化合物XU-71787を100gにナフテン酸コバルト1gを加えてN, N-ジメチルホルムアミド100gに溶解しワニスを得る。このワニスを真空乾燥し溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用い

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(8)

特開平5-78446

13

【0044】(比較例2) 4, 4'-ジフェニルメタンビスアレイミド(三井京圧) 80gと4, 4'-ジシアナミドジフェニルエーテル(マナック) 10g及び、4, 4'-ジフェニルメタンジイソシアネート(武田薬品) 10gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後真空乾燥により溶媒を除去し粉末状の試料を得た。得られた試料を厚さ2mmのスペーサを用いて*

*プレス成形により硬化物の樹脂板を得た。硬化条件は150℃で試料を、一旦、熔融した後、250℃に昇温し加圧した。得られた樹脂板の比誘電率、熱膨張率、曲げ強度、熱分解開始温度を測定した。

【0045】実施例1-5、比較例1-2で用いた化合物の硬化物特性を表1に示す。

【0046】

【表1】

表 1

	実 施 例					比 較 例	
	1	2	3	4	5	1	2
比誘電率 (1MHz)	2.8	2.7	2.7	2.7	2.9	3.0	3.6
熱膨張率 (10 ⁻⁶ ・K ⁻¹)	7.2	7.4	7.5	7.8	7.9	7.9	7.6
熱分解開始温度 (℃)	402	408	410	386	378	375	392
曲げ強度 (NN・rd)	108	104	112	106	101	109	117

【0047】(実施例6) 2, 2-ビス(4-(4-シアネートフェノキシ)フェニル)-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン80gと2, 2-ビス(4-(4-アレイミドフェノキシ)フェニル)-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン(セントラル硝子)20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ(1-ブチルパーオキシ)ヘキシン-3を0.5g 加え攪拌してワニスとして用いた。

【0048】ワニスを塗布材である日東紡製Tガラスクロス(厚さ60μm)に含浸後、150℃の恒温空気中で10分間乾燥しプリプレグを得た。得られたプリプレグ10枚を重ね、プレス中で圧力30kgf/cm²、温度130℃で30分間加熱し、さらに250℃で1時間接着硬化反応し、樹脂板を得た。樹脂ビール強度の測定用試料はプリプレグ10枚を重ねたものの両面に銅箔(古河電工製、厚さ70μm)を重ね、同様の条件で銅箔接着した。以上の方法で作製した試料について特性評価した。比誘電率は、Hewlett Packard 社製LFインピーダンスアナライザ4192Aを用い、JISC-6481に従い試料の静電容量を測定し比誘電率を計算した。銅箔ビール強度は不動工業製レオメータNR

た。樹脂成分を溶解して得た、粉末試料10mgについて、He流量100cm³/minの雰囲気中、昇温速度5℃/minにおける加熱減重曲線を測定し5%減重を示す温度を熱分解開始温度とした。熱膨張率に関しては、真空理工製熱機械特性測定装置TM-3000を用い、銅箔板から7mm×7mmに切り出した試料の厚さ方向の熱膨張率(50-220℃)測定した。昇温速度2℃/min、荷重10gの圧縮モードで測定した。可燃性の測定はUL-94により測定した。測定結果は表にまとめて示す。

【0049】(実施例7) 2, 2-ビス(4-(4-シアネートフェノキシ)フェニル)-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン80gと1-パーフルオロネニルオキシ-3, 5-フタロイルビス(4-(4-シアナミドフェノキシ)フェニル)(マナック)20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ(1-ブチルパーオキシ)ヘキシン-3を0.5g 加え攪拌してワニスとして用いた。ワニスを用いて実施例6と同様な方法で、銅箔材(デュボン社製芳香族アミド系有機合成繊維織布ケブラー49)を用いてプリプレグ、樹脂板を作製し、特性を評価した。結果を表に示す。

【0050】(実施例8) 2, 2-ビス(4-(4-シ

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(9)

特開平5-78446

15

ラル硝子) 20gとポリ(p-ビニルプロモフェニルメタクリレート) (マナック) 20gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ(1-ブチルパーオキシ)ヘキシン-3を0.2g 加え振盪保持してワニスとして用いた。このワニスを用いて実施例6と同様な方法で、誘電材(日東紡製Tガラスクロス、厚さ60μm)を用いてプリブレグ、積層板を作製し、特性を評価した。結果を表に示す。

【0051】(実施例9) 2, 2-ビス(4-(4-シアネートフェノキシ)フェニル)-1, 1, 1, 3, 3, 3-ヘキサフルオロプロパン80gと1-パーフルオロネニルオキシ-3, 5-フタロイルビス(4- *

16

* (4-シアナミドフェノキシ)フェニル) (マナック) 10g及び、ビスフェノールA型エポキシ化合物DER 323 (ダウケミカル) 10gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ(1-ブチルパーオキシ)ヘキシン-3を0.2g 加え振盪保持してワニスとして用いた。このワニスを用いて実施例6と同様な方法で、誘電材(日本アロマ製芳香族アミド系有機合成繊維不織布GAU-50 5-50)を用いてプリブレグ、積層板を作製し、特性を評価した。結果を表2に示す。

【0052】

【表2】

表 2

	実 施 例				比 較 例	
	6	7	8	9	3	4
比誘電率 (1MHz)	3.0	3.1	2.9	3.2	3.2	3.5
熱膨張率 (10 ⁻⁴ ・K ⁻¹)	7.9	8.2	8.0	8.2	8.1	7.9
ハンダ耐熱性 (Δt 300℃, 分)	≥5	≥5	≥5	≥3	≥3	≥5
難燃性 (UL-94)	V-0	V-0	V-0	V-0	V-1	V-0

【0053】(比較例3) シアネート化合物XU-71 787を100gにナフテン酸コバルト1gを加えてN, N-ジメチルホルムアミド100gに溶解しワニスを得る。このワニスを用いて実施例6と同様な方法で、誘電材(日東紡製Tガラスクロス、厚さ60μm)を用いてプリブレグ、積層板を作製し、特性を評価した。結果を表2に示す。

【0054】(比較例4) 4, 4'-ジフェニルメタンビスマレイミド(三井東圧) 80gと4, 4'-ジシアナミドジフェニルエーテル(マナック) 10g及び、4, 4'-ジフェニルメタンジイソシアネート(武田薬品) 10gをメチルイソブチルケトン100gに溶かし、100℃、60分還流下でプレポリマ化を行った。室温まで冷却後2, 5-ジメチル-2, 5-ジ(1-ブチルパーオキシ)ヘキシン-3を0.2g加え振盪保持してワニスとして用いた。ワニスを用いて実施例6と同

【0055】実施例6-9、比較例3-4で得られた積層板の特性結果を表2に示す。

【0056】(実施例10) 実施例6によりえられたプリブレグを用いて、両面に銅箔(70μm)をプレス中で圧力30kgf/cm²、温度130℃で30分間加熱し、さらに250℃で一時間接着硬化させ、銅張り積層板を得た。この銅張り積層板の両面に回路を形成し、プリブレグを介して積層接着し、LSIを搭載するピンクリッドアレイ基板を作成した。この基板は6層構造から成り、それぞれ2層の表面層、電源供給層、信号層を有する。本実施例の層構成を図1に示す。

【0057】(実施例11) 実施例6により得られたプリブレグを用い、実施例10と同様にLSIを搭載するマイクロチップキャリア基板を作成した。この基板は6層構造から成り、それぞれ2層の表面層、電源供給層、信号層を有する。

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特開平5-78446

17

源供給層10層、信号層16層、拡大量8層から成る36層構造を有する。また、この基板はマイクロチップキャリア基板を81個(9×9)搭載可能である。

【0059】(実施例13)実施例8により得られたプリプレグを用い、実施例10と同様な方法で実施例12により得られたモジュール基板を搭載する大面積基板を作成した。この基板は表面層2層、電源供給層20層、信号層24層、拡大量8層から成る54層構造をもつ。また、この基板は上記モジュール基板を64個(8×8)搭載可能である。

【0060】

【発明の効果】本発明の含フッ素樹脂は耐熱材料として優れているイミド化合物に接合性を向上させるための活性部位と、低誘電率化を計るためのフッ素基を導入した化合物フッ素シアナミドを用いたものである。フッ素基を構造中に多く取り込むことにより得られる硬化物のモル比容を増加させ、低誘電率化を図ることができた。さらにフッ素基は炭素との結合解離エネルギーが大きい *

18

*め、耐熱性の目安である熱分解温度の向上、機械的強度の向上も同時に図ることができた。また、シアナミド基は遠酸化性であることから作業性が優れる。以上、含フッ素シアナミドと含フッ素イミドから成る熱硬化性樹脂は成形性に優れ、かつ得られる硬化物は耐熱性、機械的特性に優れていることが確認できた。さらに絶縁材料の電気特性として重要な比誘電率も小さくすることができ、モールド材、配線基板、LSIの層間絶縁層等の低誘電率が要求される分野に好適な材料となることを期待できる。この多層板により構成した計算機は、絶縁層の低誘電率化及び高密度多層化が可能になり、演算実行速度が向上する。

【図面の簡単な説明】

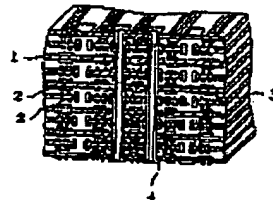
【図1】本発明の一実施例である多層プリント板の断面斜視図。

【符号の説明】

1…基板、2…回路、3…プリプレグシート、4…スルーホール。

【図1】

図 1



1…基板
2…回路
3…プリプレグシート
4…スルーホール

フロントページの続き

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技術表示箇所

(72)発明者 天羽 恒

(72)発明者 川井 良憲

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<http://nrlpubs.nrl.navy.mil/secure/submit/submit.asp?ID=1115843728471>

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特開平5-78446

(72)発明者 高橋 昭雄
茨城県日立市久慈町4026番地 株式会社日立
製作所日立研究所内

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<http://www19.ipdl.ncipi.go.jp/PA1/result/detail/main/wAAAQkaW..>

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(72)Inventor : SUZUKI MASAHIRO

NAGAI AKIRA

NISHIMURA SHIN

AMO SATORU

KAWAI YOSHINORI

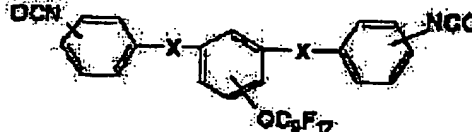
TAKAHASHI AKIO

(54) CURED MATERIAL USING FLUORINE-CONTAINING CYANATE AND LAMINATE USING THE SAME CURED MATERIAL

(57)Abstract:

PURPOSE: To obtain the subject cured material useful as an insulating material, having excellent heat-resistant and mechanical characteristics by dissolving a resin composition composed of a cyanate compound in a solvent and polymerizing under heating.

CONSTITUTION: A resin composition containing a compound of the formula (C₉H₁₇) is perfluorononyl containing one double bond; X is ester bond or ether bond) is dissolved in an organic solvent such as methyl ethyl ketone to give a uniform varnish, which is polymerized in the presence of a radical



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polymerization initiator [0.1-10 pts.wt. initiator is used based on 100 pts.wt. of the composition] such as benzoyl peroxide or dicumyl peroxide to give the objective cured material having ≤ 3 dielectric constant.

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[Claim 10] The charge of a laminated wood which used said resin constituent according to claim 1 or 2 with other resinous principles.

[Claim 11] The charge of a laminated wood obtained by carrying out laminating adhesion of the prepreg which said resin constituent according to claim 1 or 2 is infiltrated into the inorganic fiber cloth which is reinforcing materials, and is obtained.

[Claim 12] The charge of a laminated wood obtained by carrying out laminating adhesion of the prepreg which said resin constituent according to claim 1 or 2 is infiltrated into the organic fiber cloth which is reinforcing materials, and is obtained.

[Claim 13] The patchboard constituted by the charge of a laminated wood using claim 1 thru/or said resin constituent given in 12, and said resin constituent.

[Claim 14] The large area substrate constituted by the charge of a laminated wood using claim 1 thru/or said resin constituent given in 12, and said resin constituent.

[Claim 15] The module substrate constituted by the charge of a laminated wood using claim 1 thru/or said resin constituent given in 12, and said resin constituent.

[Claim 16] The microchip carrier substrate constituted by the charge of a laminated wood using claim 1 thru/or said resin constituent given in 12, and said resin constituent.

[Claim 17] The pin grid array substrate constituted by the charge of a laminated wood using claim 1 thru/or said resin constituent given in 12, and said constituent.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a fluorine-containing thermosetting resin constituent, and relates to a resin constituent suitable as a low dielectric constant insulating material which was excellent in a moldability, thermal resistance, and an adhesive property especially.

[0002]

[Description of the Prior Art] Although bismaleimide etc. has been conventionally used as a thermosetting resin constituent with thermal resistance, as for the resin by the constituent which added the bis-cyanamide to bismaleimide, it is found out that thermal resistance and a moldability are improved. (JP,58-71924,A) However, since these resin has many amide groups with large polarizability, and imide radicals, it is known that specific inductive capacity is

comparatively high. Although the resin which used fluorine-containing maleimide etc. was proposed (JP,2-73809,A), when the thermosetting resin constituent with low specific inductive capacity introduced the fluorine, it is known that an adhesive property will fall.

[0003] Moreover, a low dielectric constant ingredient has the cyanate compound (U.S. Pat. No. 4,559,399) which has aromatic series, ring type aliphatic series, or the small structure of polarization which combined these in a principal chain, and an isocyanate compound (U.S. Pat. No. 4,353,769 number). However, fire retardancy is acquired and a cyanate compound and an isocyanate compound have the fault which says that there is nothing (flammability).

[0004] Therefore, in order to use it for the multilayer board of the mainframe with which the high-speed transmission of a signal is demanded, an adhesive property and specific inductive capacity are small, and the ingredient which has fire retardancy is demanded.

[0005]

[Problem(s) to be Solved by the Invention] Although the constituent of conventional thermosetting resin had introduced the functional group which carried out the fluorine permutation as a means to reduce specific inductive capacity, this approach has the fault that an adhesive property with a metal is spoiled. Although it is generally known that what is necessary is just to introduce a functional group with polarities, such as ester, in order to improve an adhesive property, by the usual approach, specific inductive capacity becomes high.

[0006] Moreover, an isocyanate compound and a cyanate compound are quantified three times under a catalyst, and can obtain the high hardened material of crosslinking density. Moreover, although specific inductive capacity of a hardened material is low and being excelled also in dimensional stability and thermal resistance, there is a fault that the fire retardancy which is a property important as the printed circuit board is not acquired.

[0007] The purpose of this invention has low specific inductive capacity, without spoiling thermal resistance and an adhesive property, and it is in offering a further fire-resistant resin constituent.

[0008]

[Means for Solving the Problem] If this invention is outlined, specific inductive capacity is low, without spoiling thermal resistance and an adhesive property by using the fluorine-containing cyanate compound with which the rise of the specific inductive capacity by the installation can be compensated with a functional group with a polarity, and the resin constituent excellent in fire

retardancy can be offered.

[0009] (1) General formula [1]

[0010]

[Formula 4]

[0011] (-- X shows an ester bond or ether linkage for the perfluoro NONENIRU radical on which C9F17 radical ***** a double bond among a formula.) -- resin constituent which consists of the cyanate compound expressed.

[0012] (2) General formula [1]

[0013]

[Formula 5]

[0014] (-- X shows an ester bond or ether linkage for the perfluoro NONENIRU radical on which C9F17 radical ***** a double bond among a formula.) -- resin constituent which consists of at least one kind in the cyanate compound expressed and a maleimide compound, a cyanamide compound, a SHIANATO compound, an isocyanate compound, an epoxy compound, a vinyl compound, and the Pori (p-hydroxystyrene) derivative.

[0015] (3) The hardened material obtained by carrying out the heating polymerization of the uniform varnish obtained by dissolving a constituent in a solvent in claims 1 or 2.

[0016] (4) The hardened material characterized by carrying out a polymerization under existence of radical polymerization initiators, such as a peroxide, in claims 1, 2, or 3.

[0017] (5) The hardened material characterized by specific inductive capacity being three or less in claim 1 thru/or 4.

[0018] (6) General formula [1]

[0019]

[Formula 6]

[0020] (-- X shows an ester bond or ether linkage for the perfluoro NONENIRU radical on which C9F17 radical ***** a double bond among a formula.) -- electric insulator using the hardened material obtained by carrying out three-dimensions bridge formation of the resin constituent containing the cyanate compound expressed by the polymerization reaction of a multiple bond.

[0021] (7) Prepreg which a resin constituent according to claim 1 or 2 is infiltrated into the inorganic fiber cloth which is reinforcing materials, and is obtained.

[0022] (8) Prepreg which a resin constituent according to claim 1 or 2 is infiltrated into the organic fiber cloth which is reinforcing materials, and is obtained.

[0023] (9) The charge of a laminated wood using a resin constituent according to claim 1 or 2.

[0024] (10) The charge of a laminated wood which used the resin constituent according to claim 1 or 2 with other resinous principles.

[0025] (11) The charge of a laminated wood obtained by carrying out laminating adhesion of the prepreg which a resin constituent according to claim 1 or 2 is infiltrated into the inorganic fiber cloth which is reinforcing materials, and is obtained.

[0026] (12) The charge of a laminated wood obtained by carrying out laminating adhesion of the prepreg which a resin constituent according to claim 1 or 2 is infiltrated into the organic fiber cloth which is reinforcing materials, and is obtained.

[0027] (13) By the charge of a laminated wood using claim 1 thru/or a resin constituent given in

claim 12, and this constituent Patchboard constituted (14) By the charge of a laminated wood using

claim 1 thru/or a resin constituent given in 12, and this constituent Large area substrate

constituted (15) By the charge of a laminated wood using claim 1 thru/or a resin constituent

given in 12, and this constituent Module substrate constituted (16) By the charge of a laminated

wood using claim 1 thru/or a resin constituent given in 12, and this constituent Microchip carrier

substrate constituted (17) The fluorine-containing cyanate compound expressed with a general

formula [1] to claim 1 thru/or 12 in pin grid array substrate this invention constituted by the

charge of a laminated wood using the resin constituent and this constituent of a publication For

example, there are some which were shown below.

[0028]

[Formula 7]

[0029] However, it is C9F17 here. A radical has some which were shown below.

[0030]

[Formula 8]

[0031] Although the organic solvent used in this invention has a methyl ethyl ketone, methyl

isobutyl ketone, a methanol, ethanol, 3-methoxy POROPA Norian, N.N-dimethylformamide, N-methyl pyrrolidone, dimethyl sulfoxide, a trichloroethylene, etc., it should just carry out the mixed dissolution of these compounds at homogeneity.

[0032] Moreover, a radical polymerization initiator has benzoyl peroxide, JIKUMIRU peroxide, methyl-ethyl-ketone peroxide, t-butyl peroxide JIRAURE-TO, di-t-butyl peroxyphthalate, dibenzyl peroxide, 2, the 5-dimethyl -2, and 5-JI (t-butyl par oxine) hexyne-3 grade, and these are **** for 0.1 - 10 weight sections to the resin constituent 100 weight section.

[0033] the polar group which raises an adhesive property as for these compounds -- with -- in spite of being needed -- hydrogen -- comparing -- bond dissociation energy with carbon -- 100 kJ/mol Since it had the substituent with the high content of the big fluorine of molar volume greatly, it excelled in an adhesive property, fire retardancy, and thermal resistance, and it became possible to obtain thermosetting resin with low specific inductive capacity.

[0034] The moldability of resin could be raised by using these compounds as a constituent of thermosetting resin, since it had the substituent by which the fluorine permutation was carried out in coincidence, it excelled in thermal resistance, and resin with low specific inductive capacity was able to be obtained.

[0035] The thermosetting resin using a fluorine-containing cyanate compound serves as a low dielectric constant ingredient which was excellent in thermal resistance with formation and complicated three-dimensions bridge formation of the triazine ring which is a complex ring by 3 quantification reactions, such as heating. It becomes the heat-resistant insulating material which held a mechanical property, dimensional stability, etc. also at the elevated temperature by this. Moreover, since reaction by-products, such as condensation water, are not generated in this bridge formation hardening reaction, there is an advantage applicable in many fields, such as various structural materials and mold shaping. This is a different point from polyimide typical as a heat-resistant insulating material, the poly benzimidazole, polybenzothiazole, etc.

[0036]

[Function] For the rise of the dielectric constant by the polar group introduced in order to raise the adhesive property of thermosetting resin, bond dissociation energy with carbon is 100 kJ/mol from hydrogen. It became possible by introducing a substituent with the high content of the big fluorine of molar volume greatly. Thermal resistance has maintained the conventional property by holding the cyanate structure of building a three-dimensions crosslinking bond by the

polymerization reaction of a multiple bond. Furthermore, the ingredient which excelled [introduce / a substituent with the high content of a fluorine] also in fire retardancy was obtained.

[0037]

[Example] Although an example explains this invention concretely below, this invention is not limited to these examples.

[0038] <Example 1> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 100g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. The vacuum drying after cooling removed the solvent to the room temperature, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. Characterization was carried out about the obtained resin plate. Specific inductive capacity is HewlettPackard. Using shrine LF impedance analyzer 4192A, the electrostatic capacity of a sample was measured according to JIS-C -6481, and specific inductive capacity was calculated. coefficient of thermal expansion -- being related -- the product made from vacuum science and engineering -- coefficient-of-thermal-expansion (50-220 degrees C) measurement of the thickness direction of the sample started from the resin plate to 7mmx7mm using heat mechanical characteristic measuring device TM-3000 -- it carried out. It measured by the programming rate of 2 degrees C / min, and the compress mode of 10g of loads. flexural strength -- the Shimadzu make -- according to JIS-C -6481, it measured using autograph DDS-5000. They are the distance between the supporting points of 30mm, and deflection rate 2 mm/min about the sample started from the resin plate to 50mmx5mm. It measured on conditions. About pyrolysis initiation temperature, it measured using high-speed differential thermobalance TGD-7000RH made from vacuum science and engineering. It is helium flow rate of 100cm³/min about 10mg of powder samples which ground and obtained the resinous principle. The inside of an ambient atmosphere, and the programming rate of 5 degrees C / min Temperature which measures the heating loss curve which can be set and shows loss in quantity 5% was made into pyrolysis initiation temperature. A measurement result is collectively shown in a table.

[0039] <Example 2> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-

hexafluoropropane 80g and 2, 2-screw (4-(4-maleimide phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane (Central Glass) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. The vacuum drying after cooling removed the solvent to the room temperature, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0040] <Example 3> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 80g and 1-perfluoro NONENIRU oxy- 3 and 5-phthloyl screw (4-(4-cyanamide phenoxy) phenyl) (MANAC) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. The vacuum drying after cooling removed the solvent to the room temperature, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0041] <Example 4> 2 and 2-screw () [4-] (4-cyanate phenoxy) Phenyl - 1, 1, 1, 3, 3, and 3-hexafluoropropane 60g and 2, 2-screw (4-(4-maleimide phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane (Central Glass) 20g and Pori (p-vinyl BUROMO phenyl methacrylate) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was attained under 100 degrees C and 60-minute reflux (MANAC). It is 0.2g to a room temperature about after [cooling] 2, the 5-dimethyl -2, and 5-II (t-butyl par oxine) hexyne -3. In addition, the vacuum drying removed the solvent and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0042] <Example 5> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) -1, 1, 1, 3 and 3, and 3-hexafluoropropane (Central Glass) 80g and 1-perfluoro NONENIRU oxy--3 and 5-phthloyl screw (4-(4-cyanamide phenoxy) phenyl) (MANAC) 10g -- and Bisphenol A mold epoxy compound DER323 (Dow Chemical) 10g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. The vacuum drying after cooling removed the solvent to the room temperature, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0043] <Example 1 of a comparison> Naphthenic-acid cobalt 1g is added to 100g, cyanate compound XU-71787 are dissolved in 100g of N.N-dimethylformamide, and a varnish is obtained. The vacuum drying of this varnish was carried out, the solvent was removed, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0044] <Example 2 of a comparison> 4 and 4'-diphenylmethane bismaleimide (Mitsui Toatsu Chemicals)g [80] and 4 and 4'-JISHIANAMIDOJI phenyl ether (MANAC) 10g and 4,4'-diphenylmethane diisocyanate (Takeda Chemical) 10g were melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. The vacuum drying after cooling removed the solvent to the room temperature, and the powder-like sample was obtained. The resin plate of a hardened material was obtained for the obtained sample by press forming using the spacer with a thickness of 2mm. At 150 degrees C, after hardening conditions fused the sample, the temperature up of them was carried out to 250 degrees C, and they once pressurized it. The specific inductive capacity of the obtained resin plate, coefficient of thermal expansion, flexural strength, and pyrolysis temperature were measured.

[0045] The hardened material property of the compound used in the example 1-5 and the example 1-2 of a comparison is shown in Table 1.

[0046]

[Table 1]

[0047] <Example 6> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 80g and 2, 2-screw (4-(4-maleimide phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane (Central Glass) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. It is 0.5g to a room temperature about after [cooling] 2, the 5-dimethyl -2, and 5-JI (t-butyl par oxine) hexyne -3. In addition, shaking stirring was carried out and it used as a varnish.

[0048] the Nittobo T glass fabrics (60 micrometers in thickness) which are reinforcing materials about a varnish -- sinking-in coating -- carrying out -- 150-degree C constant temperature -- it dried for 10 minutes in air, and prepreg was obtained. Ten obtained prepregs were piled up, it heated for 30 minutes at pressure 30 kgf/cm² and the temperature of 130 degrees C in the press, the adhesion hardening reaction was carried out at 250 more degrees C for 1 hour, and the laminate was obtained. Although the test sample of copper foil Peel reinforcement piled up ten prepregs, it put copper foil (70 micrometers in the product made from the Koga electrical engineering, thickness) on both sides, and it carried out laminating adhesion on the same conditions. Characterization was carried out about the sample produced by the above approach. Specific inductive capacity is Hewlett Packard. Using shrine LF impedance analyzer 4192A, the electrostatic capacity of a sample was measured according to JIS-C -6481, and specific inductive capacity was calculated. Using rheometer NRM-3101D made from immobilization industry, according to JIS-C -6481, it tears off and copper foil Peel reinforcement is rate 50 mm/min. Vertical copper foil Peel reinforcement was measured on conditions. About pyrolysis initiation temperature, it measured using high-speed differential thermobalance TGD-7000RH made from vacuum science and engineering. They are the inside of the ambient atmosphere of helium flow rate of 100cm³/min, and the programming rate of 5 degrees C / min about 10mg of powder samples which ground and obtained the resinous principle. Temperature which measures the heating loss curve which can be set and shows loss in quantity 5% was made into pyrolysis initiation temperature. coefficient of thermal expansion -- being related -- the product made from

vacuum science and engineering -- coefficient-of-thermal-expansion (50 to 220 degree C) measurement of the thickness direction of the sample started from the laminate to 7mmx7mm using heat mechanical characteristic measuring device TM-3000 -- it carried out. It measured by the programming rate of 2 degrees C / min, and the compress mode of 10g of loads. Fire-resistant measurement was measured by UL-94. A measurement result is collectively shown in a table.

[0049] <Example 7> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 80g and 1-perfluoro NONENIRU oxy-- 3 and 5-phthloyl screw (4-(4-cyanamide phenoxy) phenyl) (MANAC) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. It is 0.5g to a room temperature about after [cooling] 2, the 5-dimethyl -2, and 5-JI (t-butyl par oxine) hexyne -3. In addition, shaking stirring was carried out and it used as a varnish. Using the varnish, prepreg and a laminate were produced using reinforcing materials (Du Pont aromatic amide

system organic synthesis fiber textile-fabrics Kevlar-49), and the same approach as an example 6 estimated the property. A result is shown in a table.

[0050] <Example 8> 2 and 2-screw () [4-] (4-cyanate phenoxy) Phenyl - 1, 1, 1, 3, 3, and 3-hexafluoropropane 60g and 2, 2-screw (4-(4-maleimide phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane (Central Glass) 20g and Pori (p-vinyl BUROMO phenyl methacrylate) 20g was melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux (MANAC). It is 0.2g to a room temperature about after [cooling] 2, the 5-dimethyl -2, and 5-JI (t-butyl par oxine) hexyne -3. In addition, shaking stirring was carried out and it used as a varnish. Using this varnish, prepreg and a laminate were produced using reinforcing materials (60 micrometers in the Nittobo T glass fabrics, thickness), and the same approach as an example 6 estimated the property. A result is shown in a table.

[0051] <Example 9> 2 and 2-screw (4-(4-cyanate phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 80g and 1-perfluoro NONENIRU oxy-- 3 and 5-phthloyl screw (4-(4-cyanamide phenoxy) phenyl) (MANAC) 10g and bisphenol A mold epoxy compound DER323 (Dow Chemical) 10g were melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100 degrees C and 60-minute reflux. It is 0.2g to a room temperature about after [cooling] 2, the 5-dimethyl -2, and 5-JI (t-butyl par oxine) hexyne -3. In addition, shaking stirring was carried out and it used as a varnish. Using this varnish, prepreg and a laminate were

produced using reinforcing materials (aromatic amide system organic synthesis fiber nonwoven fabric GAUmade from Japanese aroma- 505 -50), and the same approach as an example 6 estimated the property. A result is shown in Table 2.

[0052]

[Table 2]

[0053] <Example 3 of a comparison> Naphthenic-acid cobalt 1g is added to 100g, cyanate compound XU-71787 are dissolved in 100g of N.N-dimethylformamide, and a varnish is obtained. Using this varnish, prepreg and a laminate were produced using reinforcing materials (60 micrometers in the Nittobo T glass fabrics, thickness), and the same approach as an example 6 estimated the property. A result is shown in Table 2.

[0054] <Example 4 of a comparison> 4 and 4'-diphenylmethane bismaleimide (Mitsui Toatsu Chemicals)g [80] and 4 and 4'-JISHIANAMIDOJI phenyl ether (MANAC) 10g and 4,4'-

diphenylmethane diisocyanate (Takeda Chemical)-10g.were melted to methyl-isobutyl-ketone 100g, and prepolymer-ization was performed under 100-degrees C and 60-minute reflux. To the room temperature, after [cooling] 2, the 5-dimethyl -2, and 0.2g of 5-JI-(t-butyl par oxine) hexyne -3 were added, shaking stirring was carried out, and it used as a varnish. Using the varnish, prepreg and a laminate were produced using reinforcing materials (aromatic amide system organic synthesis fiber nonwoven fabric GAUmade from Japanese aroma- 505 -50), and the same approach as an example 6 estimated the property. A result is shown in Table 2.

[0055] The property result of the laminate obtained in the example 6-9 and the example 3-4 of a comparison is shown in Table 2.

[0056] <Example 10> Using the prepreg obtained according to the example 6, copper foil (70 micrometers) was heated for 30 minutes at pressure 30 kgf/cm2 and the temperature of 130 degrees C in the press to both sides, adhesion hardening was carried out at 250 more degrees C for 1 hour, and the copper-clad laminate was obtained. The circuit was formed in both sides of this copper-clad laminate, laminating adhesion was carried out through prepreg, and the pin grid array substrate in which LSI is carried was created. This substrate consists of 6 layer structures, and has a two-layer surface layer, a current supply layer, and a signal plane, respectively. The lamination of this example is shown in drawing 1 .

[0057] <Example 11> The microchip carrier substrate in which LSI is carried like an example 10

was created using the prepreg obtained according to the example 6. This substrate consists of 6 layer structures, and has a two-layer surface layer, a current supply layer, and a signal plane, respectively.

[0058] <Example 12> The module substrate carrying the microchip carrier substrate obtained by the example 11 by the same approach as an example 10 was created using the prepreg obtained according to the example 6. This substrate has 36 layer structures which consist of surface layer two-layer, ten layers of current supply layers, 16 layers of signal planes, and eight layers of expansion layers. Moreover, 81-piece (9x9) loading of a microchip carrier substrate is possible for this substrate.

[0059] <Example 13> The large area substrate carrying the module substrate obtained by the example 12 by the same approach as an example 10 was created using the prepreg obtained according to the example 6. This substrate has 54 layer structures which consist of surface layer two-layer, 20 layers of current supply layers, 24 layers of signal planes, and eight layers of expansion layers. Moreover, 64-piece (8x8) loading of the above-mentioned module substrate is possible for this substrate.

[0060] [Effect of the Invention] The fluorine-containing resin of this invention uses the combination fluorine-containing cyanamide which introduced the polar part for raising an adhesive property, and the fluorine radical for measuring low dielectric constant-ization into the imide compound which is excellent as a heat-resisting material. The molar volume of the hardened material obtained by incorporating many fluorine radicals in structure was made to increase, and low dielectric constant-ization was able to be attained. Since a fluorine radical had still larger bond dissociation energy with carbon, improvement in the pyrolysis temperature which is a heat-resistant standard, and improvement in a mechanical strength were also able to be aimed at to coincidence. Moreover, since a cyanamide radical is fast curability, workability is excellent. As mentioned above, it has checked that the thermosetting resin which consists of a fluorine-containing cyanamide and fluorine-containing imide was excellent in a moldability, and the hardened material obtained was excellent in thermal resistance and a mechanical property. Still more important specific inductive capacity as an electrical property of an insulating material can also be made small, and it can expect to become a suitable ingredient for the field as which low dielectric constants, such as an interlayer insulation film of mold material, a wiring substrate, and

LSI, are required. The reduction in a dielectric constant and high density multilayering of an insulating layer are attained, and the instruction execution rate of the computer constituted with this multilayer board improves.

TECHNICAL FIELD

[Industrial Application] This invention relates to a fluorine-containing thermosetting resin constituent, and relates to a resin constituent suitable as a low dielectric constant insulating material which was excellent in a moldability, thermal resistance, and an adhesive property especially.

PRIOR ART

[Description of the Prior Art] Although bismaleimide etc. has been conventionally used as a thermosetting resin constituent with thermal resistance, as for the resin by the constituent which added the bis-cyanamide to bismaleimide, it is found out that thermal resistance and a moldability are improved. (JP,58-71924,A) However, since these resin has many amide groups with large polarizability, and imide radicals, it is known that specific inductive capacity is comparatively high. Although the resin which used fluorine-containing maleimide etc. was proposed (JP,2-73809,A), when the thermosetting resin constituent with low specific inductive capacity introduced the fluorine, it is known that an adhesive property will fall.

[0003] Moreover, a low dielectric constant ingredient has the cyanate compound (U.S. Pat. No. 4,559,399) which has aromatic series, ring type aliphatic series, or the small structure of polarization which combined these in a principal chain, and an isocyanate compound (U.S. Pat. No. 4,353,769 number). However, fire retardancy is acquired and a cyanate compound and an isocyanate compound have the fault which says that there is nothing (flammability).

[0004] Therefore, in order to use it for the multilayer board of the mainframe with which the high-speed transmission of a signal is demanded, an adhesive property and specific inductive capacity are small, and the ingredient which has fire retardancy is demanded.

[0005]

EFFECT OF THE INVENTION

[Effect of the Invention] The fluorine-containing resin of this invention uses the combination fluorine-containing cyanamide which introduced the polar part for raising an adhesive property, and the fluorine radical for measuring low dielectric constant-ization into the imide compound which is excellent as a heat-resisting material. The molar volume of the hardened material obtained by incorporating many fluorine radicals in structure was made to increase, and low dielectric constant-ization was able to be attained. Since a fluorine radical had still larger bond dissociation energy with carbon, improvement in the pyrolysis temperature which is a heat-resistant standard, and improvement in a mechanical strength were also able to be aimed at to coincidence. Moreover, since a cyanamide radical is fast curability, workability is excellent. As mentioned above, it has checked that the thermosetting resin which consists of a fluorine-containing cyanamide and fluorine-containing imide was excellent in a moldability, and the hardened material obtained was excellent in thermal resistance and a mechanical property. Still more important specific inductive capacity as an electrical property of an insulating material can also be made small, and it can expect to become a suitable ingredient for the field as which low dielectric constants, such as an interlayer insulation film of mold material, a wiring substrate, and LSI, are required. The reduction in a dielectric constant and high density multilayering of an insulating layer are attained, and the instruction execution rate of the computer constituted with this multilayer board improves.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although the constituent of conventional thermosetting resin had introduced the functional group which carried out the fluorine permutation as a means to reduce specific inductive capacity, this approach has the fault that an adhesive property with a metal is spoiled. Although it is generally known that what is necessary is just to introduce a functional group with polarities, such as ester, in order to improve an adhesive property, by the usual approach, specific inductive capacity becomes high.

[0006] Moreover, an isocyanate compound and a cyanate compound are quantified three times under a catalyst, and can obtain the high hardened material of crosslinking density. Moreover, although specific inductive capacity of a hardened material is low and being excelled also in

dimensional stability and thermal resistance, there is a fault that the fire retardancy which is a property important as the printed circuit board is not acquired.

[0007] The purpose of this invention has low specific inductive capacity, without spoiling thermal resistance and an adhesive property, and it is in offering a further fire-resistant resin constituent.

MEANS

[Means for Solving the Problem] If this invention is outlined, specific inductive capacity is low, without spoiling thermal resistance and an adhesive property by using the fluorine-containing cyanate compound with which the rise of the specific inductive capacity by the installation can be compensated with a functional group with a polarity, and the resin constituent excellent in fire retardancy can be offered.

OPERATION

[Function] For the rise of the dielectric constant by the polar group introduced in order to raise the adhesive property of thermosetting resin, bond dissociation energy with carbon is 100 kJ/mol from hydrogen. It became possible by introducing a substituent with the high content of the big fluorine of molar volume greatly. Thermal resistance has maintained the conventional property by holding the cyanate structure of building a three-dimensions crosslinking bond by the polymerization reaction of a multiple bond. Furthermore, the ingredient which excelled [introduce / a substituent with the high content of a fluorine] also in fire retardancy was obtained.

[Brief Description of the Drawings]

[Drawing 1] The cross-section perspective view of the multilayer board which is one example of this invention.

1 [- Through hole.] -- A substrate, 2 -- A circuit, 3 -- A prepreg sheet, 4

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